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Rotational analysis of the ultraviolet band system of CS

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With 3 figures in the text

ABSTRACT

A rotational analysis of 24 bands of the ultraviolet system of CS has been made. The system arises from a transition $A\,^1\Pi$–$X\,^1\Sigma^+$. A number of perturbations are observed in the upper state arising from interactions with a $^3\Sigma^+$ and a $^3\Sigma^-$ state. At least two singlet perturbing states have also been recognized. The following constants have been derived:

State	T_0	ω_e	$\omega_e x_e$	B_e	α_e
$e\,^3\Sigma^-$	$\leqslant 39155$	$\geqslant 750$	5	$\geqslant 0.610$	0.006
$a'\,^3\Sigma^+$	$\leqslant 38858$	$\geqslant 760$	7	$\geqslant 0.585$	0.008
$A\,^1\Pi$	30798	1081.2	11.1	0.7799_5	$0.0062_9{}^a$
$X\,^1\Sigma^+$	0	1285.08	6.46	0.82005^b	0.00592^b

[a] $-0.0004_1(v+\frac{1}{2})^2$.
[b] From the microwave observations of Mockler and Bird (1955).

The dissociation energy, D''_{298}(CS), is 175 ± 7 kcal/mole.

1. Introduction

The spectrum of CS, so far as it is known at the present time, is in remarkable contrast to that of CO. Whereas in the latter molecule more than 20 electronic states have been characterized, observations on the spectrum of CS are limited to the single system in the ultraviolet region ($\lambda_{0,0} = 2575$ Å.), A–$X\,^1\Sigma^+$. A rotational analysis of two bands of this system was given some years ago by Crawford and Shurcliff (1934), who showed that it arose from a transition $A\,^1\Pi$–$X\,^1\Sigma^+$. The upper state was found to be heavily perturbed. In a later discussion of the properties of the molecules of this group, Howell (1947) suggested that this rotational analysis was incomplete, and that the upper state was perhaps $^3\Pi$. Through the kindness of Professor Crawford in sending us some of the original plates, it was possible to extend somewhat the rotational analysis (Bowen 1946, Laird 1952) and to show unambiguously, especially by the analysis of bands with $v' = 5$ which are perturbed only at $J \gtrsim 30$, that the upper state is $^1\Pi$. That the transition is allowed follows also from the observations of the spectrum in absorption (see, for example, Porter 1950), sometimes at low concentrations.

The determination of accurate rotational constants for the ground state of the molecule from observations of the microwave spectrum (Mockler and Bird 1955) encouraged us to hope that a more complete rotational analysis would be possible, to provide information about the nature of the perturbing states. Although both the distribution of intensity among the bands of the system, and the forms of the branches, particularly of the R branches, are unfavorable for detailed analyses extending over a range of values of v', some of our expectations have been fulfilled, and it has been possible to characterize two of the perturbing states.

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Table 1. Wave numbers for the 0,0, 0,1 and 0,2 bands.

J	0,0			0,1			0,2		
	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$
5				37533.35				36265.11	
6				34.67		37514.74	36275.43	64.62	
7				35.48		12.03	76.36	64.10	
8		38794.49		36.50		10.22	77.40	63.57	36251.46
9		93.47		37.18	37521.80	07.85	78.21	62.85	49.18
10		92.55		38.03	20.91	05.73	79.01	61.94	46.73
11		91.51		38.5	19.89	03.23	79.63	61.16	44.45
12		90.01		h 39.1	18.59	00.60	80.43	60.18	42.04
13		88.36		h 39.1	16.90	498.00	80.84	58.59	39.41
14						95.10	80.43		36.79
15	— *38820.14*	*89.36*		— *49.15*	*18.60*	92.02	79.63 *90.86*	*60.47*	33.79
16	*17.11*	87.00		*46.37*	*16.45*	88.61	*88.48*	*58.59*	30.70
17	*15.60*	*85.21*		*45.09*	*14.77*	84.16 *95.41*	*87.87*	*57.12*	26.67 *37.63*
18		*82.84*			*12.99*	*89.65*		*55.64*	*32.22*
19		*80.93*			*10.96*	*85.07*		*53.80*	*27.59*
20		*77.52* 85.57	*38751.09*		*07.85* 15.55	*81.31*		*50.85* 58.59	*24.32*
21		81.17	*47.66*		11.51	*77.80*		54.76	*21.23*
22		78.20	*43.89*		09.04	*74.51*		52.57	*18.04*
23		75.91	*40.25*		06.98	*71.23*		50.85	*15.12*
24		73.72	*36.56*		05.13	*67.63*		49.20	*12.06*
25	*11.87*	71.73	*32.92*		03.21	*64.36*		47.70	*08.75*
26	*11.25*	69.37	*29.31*	*43.13*	01.33	*60.88*		46.07	*05.78*
27	*10.66*	67.22	*25.53*	*42.66*	499.37	*57.55*		44.45	*02.62*
28	*09.75*	64.91	*21.76*	*42.26*	97.42	*54.02*		42.82	*199.42*
29	*09.07*	62.49	*17.89*	*41.84*	95.41	*50.48*		41.13	*96.19*
30	*08.04*	60.22	*13.67*	*41.32*	93.30	*46.75*		39.41	*92.84*
31	*07.06*	57.54	*09.43*	*40.63*	91.11	*43.04*		37.63	*89.52*
32	*06.03*	54.97	*04.81*	*39.88*	88.85	*39.30*	*86.74*	35.72	*86.15*
33	*04.74*	52.16	*01.01*	*39.04*	86.57	*35.44*	*86.35*	33.87	*82.85*
34	*03.44*	49.28	*696.83*	*38.03*	84.13	*31.53*	*85.81*	31.83	*79.15*
35	*01.98*	46.50	*92.36*	*37.24*	81.71	*27.52*	*85.33*	29.70	*75.59*
36	*00.45*	43.39	*87.86*	*36.00*	79.04	*23.39*	*84.55*	27.58	*71.96*
37	*798.82*	40.38	*83.20*	*34.75*	76.43	*19.18*	*83.76*	25.33	*68.25*
38	*96.97*	37.19	*78.59*	*33.35*	73.67	*14.91*	*82.69*	23.00	*64.32*
39	*94.58*	33.88	*73.51*	*31.57*	70.70	*10.37*	*81.55*	20.61	*60.22*
40	*91.92*	30.30	*68.48*	*29.24*	67.77	*05.71*	*79.63*	18.04	*56.08*
41		26.63	*62.90*		64.30	*00.81*		15.12	*51.66*
42		22.54	*57.01*		60.88	*395.28*		12.05	*46.58*
43		18.03			56.88			08.75	
44		12.59			51.96				

Table 2. Wave numbers for the 1,0, 1,1, 1,2 and 1,3 bands.

J	1,0			1,1			1,2			1,3		
	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$
14				38625.26								
15	39894.71			23.92			37365.88					
16	91.78			21.14		38576.04	63.25			36118.61		
17	89.14		39841.13	18.61		70.55	61.10		37313.00	16.66		36068.65
18	85.86		34.55	15.93		64.17	58.55		06.60	14.68		62.56
19	82.96		28.53	13.17		58.65	55.98		01.59	11.97		57.59
20	80.09		22.38	10.48		52.60	53.49		295.63	09.67		51.38
21	77.49		16.38	07.91		46.72	51.17		89.92	07.55		46.31
22			10.49			40.89			84.41			—
23			04.10			35.02			79.00			35.85
24												
25												
26												
27	*65.87*			*598.31*			*43.32*			*01.42*		
28	*62.68*	39819.52		*95.38*	38551.97		*40.59*	37297.36		*099.40*	36056.05	
29	*60.27*	14.73	*772.90*	*93.23*	47.65	*05.92*	*38.81*	93.30	*51.57*	*97.83*	52.32	*10.53*
30	*57.70*	10.51	*66.52*	*91.06*	43.74	*499.83*	*37.03*	89.87	*45.90*	*96.31*	49.18	*05.16*
31	*55.14*	06.53	*60.68*	*88.83*	40.22	*94.50*	*35.27*	86.70	*40.87*	*94.80*	46.33	*00.59*
32	*52.59*	02.51	*55.01*	*86.63*	36.57	*89.20*	*33.39*	83.35	*36.08*	*93.27*	43.27	*95.84*
33	*49.52*	798.34	*49.32*	*84.18*	32.78	*83.70*	*31.25*	80.04	*30.95*	*91.61*	40.49	*91.33*
34	*46.38*	93.88	*43.38*	*81.09*	28.82	*78.30*	*28.83*	76.33	*25.98*	*89.60*	37.17	*86.69*
35	*42.45*	89.05	*37.26*	*77.75*	24.33	*72.58*	*25.69*	72.44	*20.55*	*87.03*	33.56	*81.71*
36	*37.31*	83.46	*30.79*	*73.08*	19.22	*66.51*	*21.61*	67.70	*14.83*	*83.35*	29.27	*76.49*
37	*30.90*	76.99	*23.61*	*67.16*	13.21	*59.77*	*15.91*	62.03	*08.64*	*77.96*	24.10	*70.66*
38		68.99	*15.37*		05.55	*52.06*		54.95	*01.45*		17.50	*63.85*
39	55.73	58.79 *99.19*	*05.85*	92.99	495.83 *536.01*	*42.88*	42.63	45.74 *86.01*	*192.52*	105.63	08.56 *49.03*	*55.57*
40	50.09	46.35 *90.43*		87.52	483.90 *527.94*		37.88	34.20 *78.24*		01.42	35997.53 *36041.66*	
41	45.21	*82.79*	24.07	83.40	*21.05*	61.87	34.11	*71.82*	212.10	098.06	*35.80*	—
42	41.11	*76.12*	15.32	79.80	*14.63*	53.80	31.13	*65.88*	04.98	95.42	*30.39*	69.54
43	36.95	*67.45*	07.18	76.03	*06.89*	46.24	27.68	*58.84*	198.16	92.73	*23.28*	62.90
44	32.16	69.45	00.07	71.73	08.95	39.56	23.99	61.20	91.76	89.58	26.71	57.24
45	26.78	62.93	692.52	67.14	03.08	32.55	19.90	55.89	85.26	85.54	21.90	51.37
46	*32.16*	57.53	84.53	*73.09*	498.16	25.16	*26.34*	51.36	78.50	*92.71*	18.10	44.96

Table 2 (continued)

J	1,0			1,1			1,2			1,3		
	R(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)
47	*39827.45*	39751.99	39676.01	*38568.58*	38493.29	38417.27	*37322.51*	37247.14	37170.99	*36089.60*	35914.21	—
48	*23.43*	46.37	*78.28*	*65.16*	88.13	*19.98*	*19.55*	42.61	*74.44*	*87.16*	10.26	*36042.17*
49	*19.51*	38.96 *47.98*	*70.12*	*62.13*	81.24 *90.51*	*12.23*	*16.97*	36.33 *45.84*	*67.40*	*85.15*	04.62 —	*35.67*
50	*15.92*	*39.97*	*62.83*	*58.72*	*83.00*	*05.76*	*14.54*	*38.63*	*61.39*	*83.35*	—	*30.26*
51	*12.12*	*33.69*	*55.97*	*55.62*	*77.17*	*399.44*	*11.92*	*33.45*	*55.69*	*81.40*	*02.97*	*25.10*
52	*08.27*	*28.11*	*48.95*	*52.50*	*72.18*	*93.11*	*09.46*	*29.16*	*50.00*	*79.31*	*35999.21*	*20.09*
53	*04.20*	*22.64*	*42.13*	*49.17*	*67.35*	*86.90*	*06.60*	*24.88*	*44.34*	*77.32*	*95.54*	*15.09*
54		*17.16*	*35.08*		*62.55*	*80.51*		*20.56*	*38.63*		*91.96*	*09.91*
55		11.81	*28.02*		58.05	*74.11*		16.76	*32.87*		88.73	*04.84*
56		06.01			52.69			12.10			84.77	
57		00.07			47.60			07.61			80.97	
58		694.05			42.18			03.02			76.97	
59		88.01			36.81			198.26			73.08	
60		81.66			31.27			93.42			68.91	
61		75.04			25.29			88.25			64.36	
62		68.16			19.16			82.76			59.55	
63		60.38			12.10						54.24	

Table 3. Wave numbers for the 2,1, 2,2, 2,3 and 2,4 bands.

J	2,1			2,2			2,3			2,4		
	R(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	(*QJ*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)
6		39607.97									35869.26	
7		07.20			38348.06						68.92	
8	39619.93	06.39		38361.04	47.38			37101.26		35881.95	68.27	
9	20.62	05.46		61.85	46.59		37115.79	00.47		82.80	67.59	
10		04.32	39589.24	62.34	45.73	38330.79	16.38	099.68		83.63	67.07	35851.96
11		03.11	86.49	62.96	44.62	28.00	17.08	98.88	37082.17	84.18	66.25	49.47
12		01.85	83.50	63.2	43.47	25.37	17.39	97.78	79.57	[illegible]	[illegible]	[illegible]

18	18.48	89.67	63.97	61.04	32.39	06.38	16.32	87.09	62.08	[illegible]	[illegible]	[illegible]
19	16.09	85.71	59.75	59.12	28.62	02.74	14.79	84.33	58.34	83.63	53.26	27.41
20	12.94	80.86	55.16	56.04	22.87	298.35	11.93	79.38	54.20	80.99	48.49	23.54
21		*95.02*	49.76		*38.32*	93.23			49.20			18.80
22		*89.67*	43.13		*33.41*	86.86		*89.73*	43.11		*59.38*	12.88
23		*85.22*			*29.20*			*85.76*			*55.80*	
24		*79.71*						*80.57*			*51.0*	
25		99.39										
26	*23.00*	90.87		*68.04*	36.00		*25.24*				64.15	
27		83.50		*66.19*	28.62		*23.99*	86.41		*95.06*	57.62	
28	*19.27*	77.71	*33.73*	*64.89*	22.97	*79.48*	*22.99*	81.28	*37.54*	*94.50*	52.78	*08.88*
29	*17.67*	73.16	*28.75*	*63.54*	19.10	*74.72*	*22.04*	77.68	*33.07*	*93.87*	49.47	*04.75*
30	*16.09*	69.63	*23.91*	*62.26*	15.95	*70.08*	*21.09*	74.78	*29.00*	*93.30*	46.96	*01.10*
31	*14.47*	66.33	*18.99*	*61.04*	12.84	*65.73*	*20.10*	72.06	*24.73*	*92.76*	44.67	*797.39*
32	*12.33*	62.91	*14.27*	*59.10*	09.81	*61.22*	*18.86*	69.44	*20.77*	*91.67*	42.35	*93.82*
33	11.01	58.98 *60.45*	*09.39*	58.30	06.48 *07.81*	*56.67*	18.17	66.35 *67.64*	*16.80*	91.67	39.69 *41.06*	*90.02*
34	09.07	*56.13*	*04.02*	56.86	*03.84*	*51.78*	17.10	*64.26*	*12.13*	90.93	*38.07*	*85.93*
35	07.20	*52.61*	499.51	55.26	*00.83*	47.63	15.91	*61.63*	08.45	90.19	*35.79*	82.64
36	05.10	*48.99*	94.41	53.57	*297.56*	42.96	14.79	*58.81*	04.13	89.30	*33.41*	78.79
37	02.89	*45.29*	89.06	51.82	*94.46*	38.28	13.55	*55.96*	36999.84	88.54	*30.99*	74.95
38	00.54	*41.51*	83.89	49.96	*91.14*	33.39	12.01	*53.04*	95.48	87.62	*28.59*	70.94
39	598.05	*37.59*	78.43	48.06	*87.63*	28.39	10.59	*50.08*	90.99	86.53	*26.10*	66.99
40	95.60	*33.73*	72.94	45.86	*84.03*	23.38	08.85	*47.14*	86.48	85.59	*23.55*	62.87
41	92.76	*29.56*	67.41	43.63	*80.43*	18.33	07.29	*43.95*	81.85	84.18	*20.80*	58.76
42	89.87	*25.38*	61.63	41.36	*76.71*	13.06	05.33	*40.67*	77.08	82.80	*18.12*	54.55
43	86.57	*20.88*	55.72	38.32	*72.77*	07.64	02.99	*37.27*	72.20	81.00	*15.20*	50.13
44		*16.09*	49.57		*68.56*	02.13		*33.58*	67.15		*12.04*	45.47
45		12.02	43.06		65.08	196.07		30.66	61.61		09.63	40.69
46		07.11			60.59			26.71			06.29	
47		01.88			56.05			22.73			02.79	
48		496.41			51.14			18.32			798.98	
49		90.32			45.60			13.47			94.61	
50		82.93			38.82			07.22			89.05	
51		72.92 *500.96*			29.21 *57.44*			36998.23 *26.59*			— *808.87*	
52		*488.95*			*45.72*			*15.54*			—	
53		*80.16*			*37.76*			*08.13*			*791.79*	
54		*72.88*			*31.16*			*02.00*			*86.40*	
55		*64.34*			*23.38*			*36994.90*			*79.84*	
56		*54.04*			*13.72*							

Table 4. Wave numbers for the 3,2, 3,3, 3,4 and 3,5 bands.

J	3,2			3,3			3,4			3,5		
	R(J)	Q(J)	P(J)	R(J)	Q(J)	P(J)	R(J)	Q(J)	P(J)	R(J)	Q(J)	P(J)
4				38127.84								
5				28.86	38119.94							
6				29.81	19.40							
7				30.71	18.65							
8		39363.92		31.27	17.91		36898.55			35678.50	35664.95	
9		62.89	39349.39	32.23	17.09		99.29			79.33	64.38	
10		61.93	47.05	32.69	16.15	38101.11	900.02	36883.21	36868.37	80.06	63.70	35648.65
11		60.79	44.24	33.24	15.18	098.51	00.53	82.55	66.02	—	62.80	46.28
12		59.61	41.33		14.07	96.02	01.19	81.57	63.71	81.05	62.11	43.90
13	h 39379.4	58.26	38.49		12.86	93.28	01.62	80.58	60.86	81.57	61.27	41.62
14	h 79.4	56.72	35.69		11.50	90.6		79.46	58.27	82.38	60.24	39.17
15		55.21	32.44		10.15	87.63		78.24	55.56	83.20	59.29	36.52
16		53.65	29.46		08.71	84.56		76.95	53.06	83.70	58.13	34.15
17		51.77	26.20		07.15	81.65	h 02.7	75.59	50.00		57.00	31.36
18		49.94	22.28		05.41	78.42	h 02.7	74.15	47.04	h 84.4	55.72	28.71
19	77.98	47.92	19.10		03.62	74.90	h 02.7	72.61	43.93	h 84.4	54.40	25.46
20	77.26	45.74	15.69	33.24	01.85	71.51		70.84	40.83	h 84.4	52.99	22.76
21	76.35	43.52	12.00	32.69	099.67	68.00		69.15	37.59		51.51	19.98
22	75.00	41.12	08.10		97.73	64.50		67.30	34.17	83.70	49.83	16.94
23		38.50	04.01		95.34	60.69		65.25	30.71		48.09	13.55
24		*36.44*	299.31		*93.60*	56.63		*63.82*	26.76		*46.98*	09.77
25		*33.54*		*32.72*	*90.90*		*03.53*	*61.54*			*44.82*	
26	*72.86*	*30.46*		*30.71*	*88.21*		*01.62*	*59.01*		*86.92*	*42.75*	
27	*71.21*	*27.17*	*90.35*	*29.30*	*85.16*	*48.39*	*00.53*	*56.29*	*19.53*	*85.30*	*40.18*	*03.67*
28	*69.49*	*23.39*	*84.76*	*27.84*	*81.65*	*43.01*	*899.29*	*53.12*	*14.45*	*84.39*	*37.55*	*598.93*
29	*67.56*	*17.64* 30.39	*79.70*	*26.22*	*76.33* 88.96	*38.40*	*98.03*	*48.29* 60.86	*10.19*	*83.76* *82.69*	*32.94* 45.50	*94.98*
30	*65.29*	23.82	*74.79*	*24.24*	82.87	*33.49*	*96.38*	54.93	*05.94*	*81.55*	40.18	*91.06*
31	*61.93*	19.01	*69.61*	*21.27*	78.49	*28.85*	*93.70*	50.97	*01.47*	*79.31*	36.52	*87.04*

36	53.65 *56.55*	299.21	46.15	15.18 *17.91*	60.69	07.66	89.99 *92.31*	35.17	82.12	77.66 *80.08*	22.63	69.69
37	*52.94*	*96.97*	40.04	*14.99*	*58.87*	01.92	*89.99*	*33.81*	77.00	*77.66*	*21.75*	64.89
38	*49.94*	*91.86*	33.17 *36.27*	*12.38*	*54.11*	37995.64 *98.65*	*87.79*	*29.55*	— *74.09*	*76.24*	*17.96*	— *62.52*
39	*47.05*	*87.34*	*29.59*	*10.12*	*50.13*	*92.32*	*85.77*	*26.04*	*68.52*	*74.60*	*14.87*	*57.10*
40	*44.08*	*82.82*	*23.52*	*07.15*	*45.98*	*86.80*	*83.54*	*22.40*	*63.08*	*72.94*	*11.72*	*52.49*
41	*40.65*	*78.09*	*17.35*	*04.36*	*41.78*	*81.15*	*81.26*	*18.65*	*57.97*	*71.10*	*08.45*	*47.86*
42	*36.74*	*72.90*	*11.05*	*01.11*	*37.10*	*75.35*	*78.30*	*14.45*	*52.77*	*68.79*	*04.77*	*43.10*
43	*32.45*	*67.20*	*04.50*	*097.19*	*31.82*	*69.32*	*74.99*	*09.77*	*47.16*	*65.67*	*00.59*	*37.99*
44	*26.20*	*60.05*	*197.64*	*91.58*	*25.10*	*62.92*	*70.02*	*03.69*	*41.21*	*61.27*	*594.98*	*32.63*
45		*48.77* 80.81	*90.01*		*14.55* 46.76	*55.73*		*793.37* 25.34	*34.67*		*85.41* 17.25	*26.44*
46		*32.39* 67.20	*80.69*		*37998.65* 33.63	*47.17*		*78.44* 13.13	*26.49*		*70.81* 05.59	*19.06*
47	34.44	57.96		101.11	24.86		81.34	04.88		74.32	597.83	
48	27.28	50.47		094.92	17.97		75.59	798.54		69.04	92.11	
49	22.25	43.18	79.35	90.1	11.21	47.17	71.45	92.34	28.42	65.67	86.51	22.46
50	17.61	33.17 *50.70*	69.45	86.16	01.92 *19.59*	37.85	67.88	83.72 *01.35*	19.80	62.70	78.41 *95.96*	14.47
51	13.00	*38.53*	61.02	82.39	*07.64*	30.17	64.56	*790.07*	12.59	59.97	*85.41*	07.89
52	08.62	*30.87*	53.13	78.49	*00.75*	22.91	61.54	*83.72*	05.75	57.35	*79.77*	01.81
53	04.11	*24.41*	45.38	74.80	*37994.83*	15.89	58.27	*78.52*	699.58	54.84	*75.09*	496.12
54	299.35	*18.18*	37.81	70.27	*89.28*	09.02	54.93	*73.53*	93.15	52.14	*70.84*	90.47
55	*95.15*	*11.88*	30.27	*66.74*	*83.66*	02.03	*51.96*	*68.56*	87.02	*49.84*	*66.47*	84.92
56	*90.58*	05.87	22.58	*62.80*	78.42	894.96	*48.18*	63.97	80.68	*46.98*	62.50	79.05
57	*85.78*	199.64	*15.27*	*58.87*	72.58	*88.30*	*45.26*	59.07	*74.60*	*44.53*	58.32	*73.76*
58	*80.80*	93.36	*07.40*		67.24	*81.02*	*41.64*	54.14	*68.10*	*41.55*	54.03	*67.92*
59	*76.04*	86.90	*099.53*		61.51	*74.09*		49.15	*61.56*		49.63	*62.21*
60	*70.94*	80.52	*91.56*		55.72	*67.17*		44.04	*55.23*		45.32	*56.42*
61		73.83	*83.45*		49.84			38.90			40.96	
62		67.17	*75.31*		43.84			33.60			36.46	
63		60.21			37.86			28.42			31.89	
64		53.31			31.49			22.79			27.31	
65		46.23			25.15			17.34			22.41	
66		38.81			18.61			11.62			17.33	
67		31.37			11.95			05.75			12.25	
68		23.19			04.56			699.57			07.02	

Table 5. Wave numbers for the 4,2, 4,3, 4,5 and 4,6 bands.

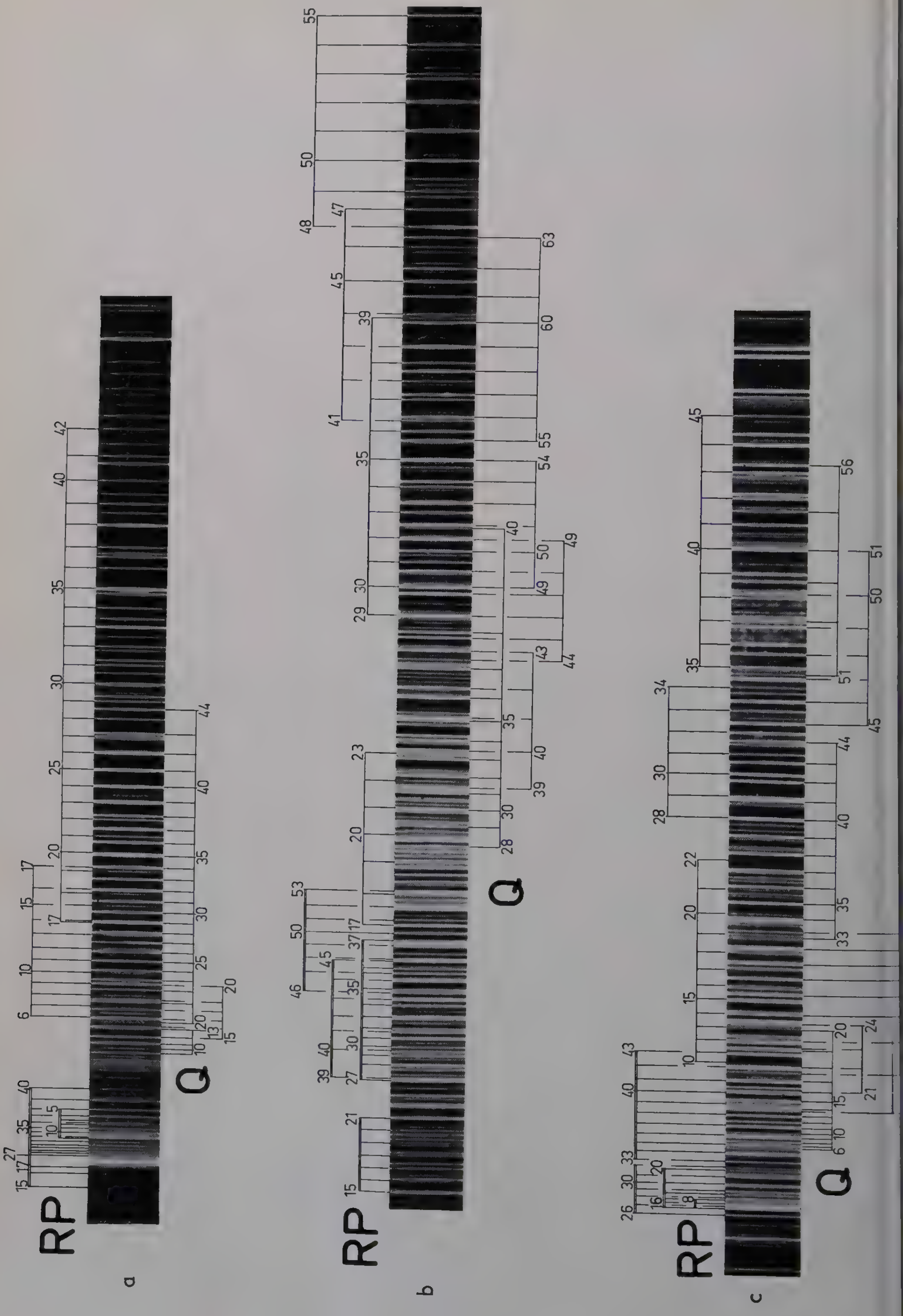
J	4,2			4,3			4,5			4,6		
	R(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)	*R*(*J*)	*Q*(*J*)	*P*(*J*)
5					39105.61			36651.81			35444.40	
6					04.69						43.72	
7	h 40360.9				03.72			51.31			43.08	
8	h 60.9	40348.18		h 39115.5	02.66			49.18			42.23	
9	h 60.9	46.60		h 15.5	01.19		h 36662.7	48.23			41.13	
10	h 60.9	44.99		h 15.5	099.76		h 62.7	46.86		h 35455.99	39.92	
11	60.56	43.18	40327.28	h 15.5	98.17	39082.23	h 62.7	45.54	36630.03	h 55.99	38.77	
12	59.95	41.14	23.99		96.29	78.91		43.91	26.64		37.62	35420.01
13	58.95	38.96	20.27	14.22	94.08	75.43	62.31	42.24	23.45		35.70	16.65
14	57.78	36.42	16.30	13.46	91.79	71.72	61.39	40.11	19.99		33.81	13.54
15	56.22	33.61	12.29	11.62	89.09	67.84	60.43	37.76	16.50		31.86	10.38
16	54.34	30.44	07.96	09.91	86.12	63.66	58.76	35.17	12.59		29.23	06.46
17	51.83	26.93	03.11	07.53	82.47	58.75	57.04	32.07	08.53		26.47	02.85
18	48.35	22.76	297.76	04.69	78.52	53.93	54.45	28.58	03.41		23.16	398.03
19		17.74	92.11		74.22	48.67		24.53	598.61		19.23	
20		12.29	85.80		69.16	42.48		19.80	93.17		14.64	
21		06.09			62.89			14.05			09.29	
22		298.76 *349.98*			55.80 *106.90*			07.72 *658.77*			03.11 *54.33*	
23		90.59 *42.07*			47.78 *099.55*			599.98 *51.81*			395.57 *47.57*	
24		*35.52*			*93.24*			*46.18*			*42.23*	
25		*29.76*			*87.72*			*41.30*			*37.62*	
26	*69.87*	*23.99*		*28.20*	*82.19*		*82.38*	*36.43*		*79.05*	*33.06*	
27	*66.04*	*17.74* 337.19		*24.69*	*76.38* 95.61		*79.54*	*31.15* 650.40		*76.54*	*28.03* 447.57	
28	*62.57*	*10.21* 27.13	*81.57*	*21.60*	*69.08* 86.12	*40.37*	*76.92*	*24.53* 41.30	*95.81*	*74.31*	*21.83* 38.77	*93.19*
29	*59.20*	*00.14* 19.02	*74.46*	*18.74*	*59.57* 78.33	*33.72*	*74.88*	*15.63*	*89.87*	*72.39*	*13.16*	*87.38*

33	*47.24*	297.76	*49.09*	*07.98*	58.42	*09.79*	*67.10*	17.62	*69.01*	*66.30*	16.65	*68.06*
34	*44.40*	92.94	*42.93*	*04.69*	54.11	*03.99*	*65.08*	14.03	*63.95*	*64.53*	13.54	*63.41*
35	*41.09*	88.24	*36.61*	*02.05*	50.10	*38998.13*	*63.40*	10.65	*58.96*	*63.27*	10.38	*58.85*
36	*37.78*	83.46	*30.28*	*099.67*	45.43	*92.21*	*61.62*	07.05	*53.77*	*61.84*	07.43	*54.0*
37	*34.26*	78.65	*24.27*	*96.96*	41.03	*86.19*	*59.49*	03.47	*48.91*	*60.23*	04.26	*49.74*
38	*31.12*	73.59	*17.58*	*94.13*	36.57	*80.52*	*57.39*	599.94	*43.89*	*58.57*	01.20	*45.16*
39	*27.41*	68.60	*10.99*	*90.87*	31.95	*74.43*	*55.19*	96.25	*38.85*	*56.93*	398.03	*40.43*
40	*23.99*	63.49	*04.57*	*87.72*	27.48	*68.28*	*53.02*	92.60	*33.56*	*55.20*	94.81	*35.79*
41	*20.27*	58.26	*197.80*	*84.48*	22.56	*62.06*	*50.6*	88.79	*28.36*	*53.20*	91.50	*31.08*
42	*16.31*	52.91	*91.13*	*81.12*	17.69	*55.73*	*48.31*	85.01	*23.01*	*51.38*	88.15	*26.19*
43	*12.29*	47.41	*84.22*	*77.60*	12.79	*49.41*	*46.0*	80.96	*17.67*	*49.57*	84.73	*21.27*
44	*07.96*	41.88	*77.15*	*74.00*	07.72	*42.64*	*43.26*	76.93	*12.06*	*47.57*	81.23	*16.25*
45	*03.77*	36.19	*69.69*	*70.19*	02.49	*36.29*	*40.58*	72.88	*06.62*	*45.46*	77.60	*11.25*
46	*299.23*	30.28	*62.53*	*66.23*	38997.17	*29.44*	*37.76*	68.69	*01.01*	*43.08*	73.97	*06.17*
47	*94.69*	24.27	*55.10*	*62.02*	91.76	*22,53*	*34.67*	64.32	*495.16*	*40.55*	70.28	*01.04*
48	*89.48*	18.13	*47.66*	*57.63*	86.19	*15.48*	*31.15*	59.87	*89.27*	*37.62*	66.37	*295.71*
49	*84.03*	11.79	*39.64*	*52.61*	80.52	*08.36*	*27.56*	55.31	*83.24*	*34.35*	62.35	*90.16*
50	*75.96*	05.28	*31.70*	*45.40*	74.38	*00.70*	*21.15*	50.63	*76.81*	*28.6*	58.07	*84.41*
51		198.52	*22.82*		68.25	*892.60*		45.59	*69.97*		53.79	*77.85*
52		91.13	*11.52*		61.78	*81.96*		40.29	*60.43*		49.00	*69.05*
53		83.44			54.46			34.31			43.74	
54		73.84 *98.58*			45.46 *70.13*			26.55 *51.45*			36.70 *61.47*	
55		58.87 *81.03*			31.12 *53.26*			13.52 *35.84*			24.18 *46.57*	
56		*69.69*			*42.73*			*26.37*			*37.67*	
57		*60.38*			*33.90*			*19.09*			*31.08*	
58		*51.19*			*25.51*			*12.06*			*24.73*	
59		*39.64*			*14.61*			*02.59*			*16.03*	
60		*20.50* 43.54			*896.60* 919.37			*485.93* 508.56			*299.65* 322.80	
61		31.70			08.36			499.06			13.75	
62		22.13			899.42			91.65			07.26	
63		12.35			90.38			84.12			00.48	
64		01.30			80.06			75.18			292.37	

Table 6. Wave numbers for the 5,3, 5,4, 5,6 and 5,7 bands.

J	5,3			5,4			5,6			5,7		
	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$
4				38856.28								
5				57.05	38848.20							
6				57.75	47.40	38838.75	36429.74					
7				58.35	46.45	36.64	30.59	36418.83				
8		40078.31			45.42	33.61	31.28	18.02				
9		77.10			44.44	30.94	31.87	17.14				
10	40092.0	75.68	40061.15	h 59.4	43.22	28.59	32.41	16.16			35222.22	
11	h 92.0	74.31	57.90	h 59.4	41.86	25.74		15.22			21.26	35205.20
12		72.87	55.30	h 59.4	40.42	22.70		13.89	36396.50		20.16	02.49
13		71.29	52.08		38.99	20.16		12.72	93.68		19.04	
14	91.19	69.10	48.66		37.23	17.00		11.56	91.01		17.88	
15	90.58	67.10	45.13	59.01	35.28	13.63		09.95	87.90		16.57	194.33
16	89.92	65.09	41.59	58.35	33.61	10.50		08.32	84.53		15.24	91.79
17	89.09	62.91	38.06	57.75	31.47	06.40		06.75	81.66		13.82	88.94
18	88.15	60.41	34.17	57.05	29.29	02.89		05.01	78.52		12.36	86.06
19	87.13	57.90	30.14	56.28	26.87	798.91	32.41	03.16	75.32		10.71	82.94
20	86.01	55.30	25.96	55.18	24.66	95.32	31.78	01.20	71.87		08.99	
21	84.55	52.54	21.90	54.27	22.01	91.28	31.28	399.15	68.42	35239.24	07.08	76.34
22	83.17	49.48	17.39	52.86	19.42	86.88	30.59	97.00	64.79	38.83	05.26	73.04
23	81.51	46.48	12.88	51.43	16.62	82.78	29.74	94.77	60.92	38.39	03.41	69.66
24	79.53	43.34	08.31	49.89	13.63	78.55	28.79	92.40	57.23	37.60	01.30	66.10
25	77.65	39.98	03.20	48.33	10.50	73.84	27.64	89.91	53.26	36.81	199.03	62.34
26	75.56	36.53	39998.45	46.40	07.17	69.30	26.33	87.34	49.30	35.83	96.79	58.68
27	72.87	32.63	93.19	44.41	03.68	64.57	24.96	84.53	45.23	34.82	94.33	54.75
28	70.18	28.85	87.79	41.86	00.27	59.25	23.02	81.66	40.64	33.26	91.79	50.69
29	67.10	24.66	82.23	38.99	796.67	54.31	21.11	78.52	35.98	31.33	88.94	46.58
30	63.07	20.35	76.22	35.35	92.54	48.38	18.02	75.32	31.28	28.89	86.03	41.91
31	57.90	15.76	69.82	30.32	88.38	42.48	13.86	71.87	25.96	24.90	82.94	37.12
32	50.51	10.75	62.79		83.59	35.66	07.48	67.97	19.98	19.04	79.49	31.50
33		05.36	54.13		78.55	27.61		63.65	12.55		75.61	24.40

36		82.23 *14.70*			56.86 *789.36*			44.25 *76.90*			57.55 *190.08*	
37		70.57 *04.44*			45.66 *79.59*			33.85 *67.98*			47.54 *81.46*	
38		56.20 *39996.07*			31.88 *71.50*			21.02 *60.83*			35.18 *74.77*	
39		40.29 *88.68*			16.53 *64.56*			06.62 *54.79*			21.33 *69.32*	
40		23.21 *81.72*			699.85 *58.18*			290.91 *49.30*			06.04 *64.29*	
41		*75.08*			*52.09*			*44.25*			*59.63*	
42		*68.32*			*45.66*			*38.78*			*54.75*	
43		*60.53*			*38.42*			*32.53*			*49.11*	
44		*50.64*						*24.46*			*41.91*	
45												
46		51.60			31.38			328.48			46.58	
47		40.27			20.50			18.87			37.63	
48		31.49			12.10			11.74			30.95	
49		22.45			03.84			04.48			24.40	
50		12.29			694.30			295.99			16.53	
51		899.70 *942.73*			82.18 —			— *328.48*			06.48 —	
52		*26.86*			—			*14.42*			*36.02*	
53		*14.18*			*98.04*			*03.57*			*25.91*	
54		*03.62*			*88.07*			*295.01*			*18.01*	
55		*984.43*			*79.44*						*11.30*	
56		*85.79*			*71.25*						*05.25*	
57		*77.20*			*63.78*						*099.46*	
58		*68.78*			*55.94*						*93.85*	
59		*60.20*			*48.26*						*88.25*	
60		*51.95*			*40.29*						*82.57*	
61		*43.39*			*32.57*						*76.99*	
62		*34.65*			*24.85*						*71.36*	
63		*26.03*									*65.46*	
64		*17.06*									*59.72*	
65		*08.23*									*53.80*	
66		*00.07*									*47.48*	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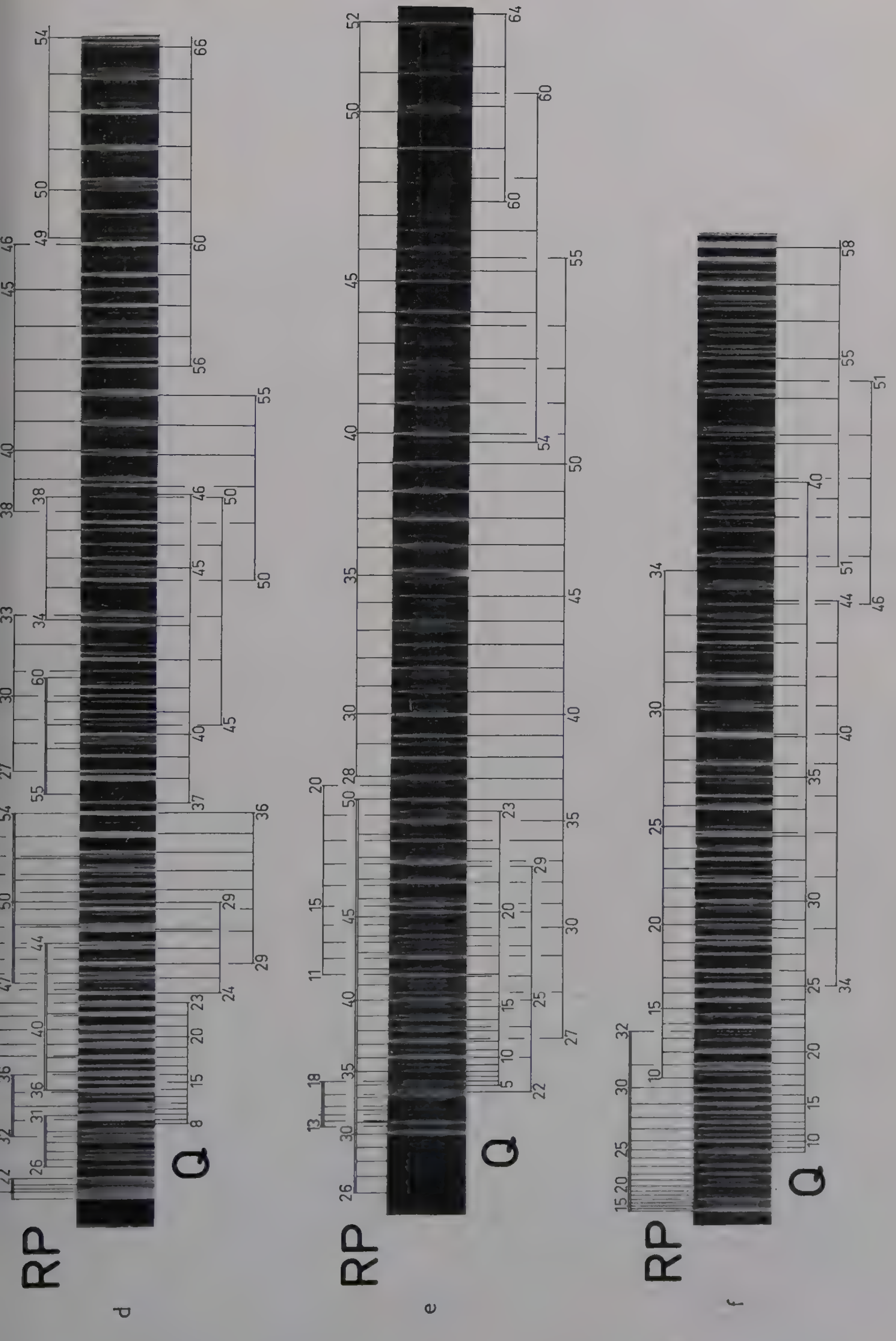

Fig. 1. Reproductions of typical bands. (*a*) 0,1, (*b*) 1,2, (*c*) 2,1, (*d*) 3,2, (*e*) 4,3, (*f*) 5,3.

2. Experimental

The spectrum was excited by an a.c. discharge through a stream of carbon disulphide vapour in a silica tube of conventional pattern. Observation was confined largely to the positive column. Photographs were taken in both first and second orders of a 21 ft Wood grating with 165000 lines. Exposure times for the first order plates, which were used for the analysis, were between $1\frac{1}{2}$ and 3 hours.

3. Analysis

Structure of the bands

The bands have the normal structure of a $^1\Pi$–$^1\Sigma$ transition, but all the upper vibrational levels are perturbed and in consequence the analysis has in some places been rather difficult to perform. This is especially the case with bands having $v' = 1$. In all, 24 bands have been analysed, namely: 0,0, 0,1, 0,2, 1,0, 1,1, 1 2, 1,3, 2,0, 2,1, 2,2, 2,3, 2,4, 3,2, 3,3, 3,4, 3,5, 4,2, 4,3, 4,5, 4,6, 5,3, 5,4, 5,6 and 5,7. The wave numbers for all band lines, except those for 2,0, which is the weakest band on our plates, are given in Tables 1–6. Each band was measured at least twice. The relative accuracy of the measurements of lines free from overlapping is about ± 0.05 cm^{-1}. In some places we found small displacements, not, however, large enough to affect the analysis, in the absolute wave numbers arising from the use of weak comparison lines. Fig. 1 gives reproductions of some of the bands.

Determination of rotational constants

For the ground state, $X\,^1\Sigma^+$, we have used the rotational constants derived by Mockler and Bird, thus:

$$B_v'' = 0.82005–0.00592\,(v'' + \tfrac{1}{2})\ \text{cm}^{-1}$$
$$D'' = 1.34 \times 10^{-6}\ \text{cm}^{-1}\ \text{(taken from Kratzer's relation).}$$

The rotational constants for the $^1\Pi$ state were determined in the following way. From the B''–B' curves (see § 4 and fig. 2) B''–B' was determined at J values where the perturbations are least. The small correction for centrifugal stretching ($2\,\Delta\,DJ^2$), was added. D', from Kratzer's relation, is 1.62×10^{-6} cm^{-1}. The values of B' follow the equation

$$B_v' = 0.7799_5–0.0062_9\,(v + \tfrac{1}{2}) - 0.0004_1\,(v + \tfrac{1}{2})^2.$$

Table 7 gives the observed and calculated B' values. The discrepancy for $v' = 1$ arises from the influence of strong perturbations.

Determination of vibrational constants

The constants for the upper level were derived as follows. For two Q lines with the same value of J from bands with different v' (v_1' and v_2') but with the same value of v'', we have

$$\omega_e'\,(v_1' - v_1') - \omega_e' x_e'\,(v_1'^2 + v_1' - v_2'^2 - v_2') = Q\,(J)_{v_1} - Q\,(J)_{v_2} + (B_{v_2'} + B_{v_1'})\,J\,(J+1).$$

For the unperturbed parts of the upper levels these equations were formed for all $v_1' v_2'$ combinations. ω_e' and $\omega_e' x_e'$ were then calculated by the method of least squares. The constants derived are:

Table 7. Rotational constants for the $^1\Pi$ state.

v	B'_{obs}	B'_{calc}
0	0.7767	0.7767
1	0.7683	0.7696
2	0.7619	0.7617
3	0.7528	0.7529
4	0.7430	0.7433
5	0.7333	0.7330

$D' = 1.62 \times 10^{-6}$ cm^{-1}.

$$\omega'_e = 1081.20, \qquad \omega'_e x'_e = 11.1.$$

For the lower state similar equations were formed for Q lines from bands with different lower v'' numbers (v''_1 and v''_2) but with the same upper level v'. As for the upper level the equations were set up for all available $v''_1 v''_2$ combinations and the determination of ω''_e and $\omega''_e x''_e$ was made in the same way. The accuracy of the constants here is very good, as the lower state is unperturbed. The constants are:

$$\omega''_e = 1285.08, \qquad \omega''_e x''_e = 6.46.$$

ν_e has been determined from these vibrational constants and from ν_0 values calculated from

$$\nu_0 = Q(J) + (B'' - B')J(J+1) + (D' - D'')J^2(J+1)^2.$$

The result is $\nu_e = 38898$ cm^{-1}.

The origins are given in Table 8.

4. Perturbations

Detection of the perturbations

The upper vibrational levels are all strongly perturbed. In order to follow the course of the perturbations the following expressions were used (see for example Lagerqvist, Nilheden and Barrow, 1952):

Table 8. Origins of analyzed bands in cm^{-1}.

v' \ v''	0	1	2	3	4	5	6	7
5				40083.1_8	38849.9_5		36421.9_2	35226.6_6
4			40365.6	39119.7		36665.5	35458.1	
4			39376.0_1	38129.7_2	36896.1_0	35675.8_6		
2	40887.2_4	39615.5_1	38356.3_3	37109.6_1	35876.2_0			
1	39860.4	38588.7	37329.3	36082.8				
0	38797.8	37525.6_3	36266.2_8					

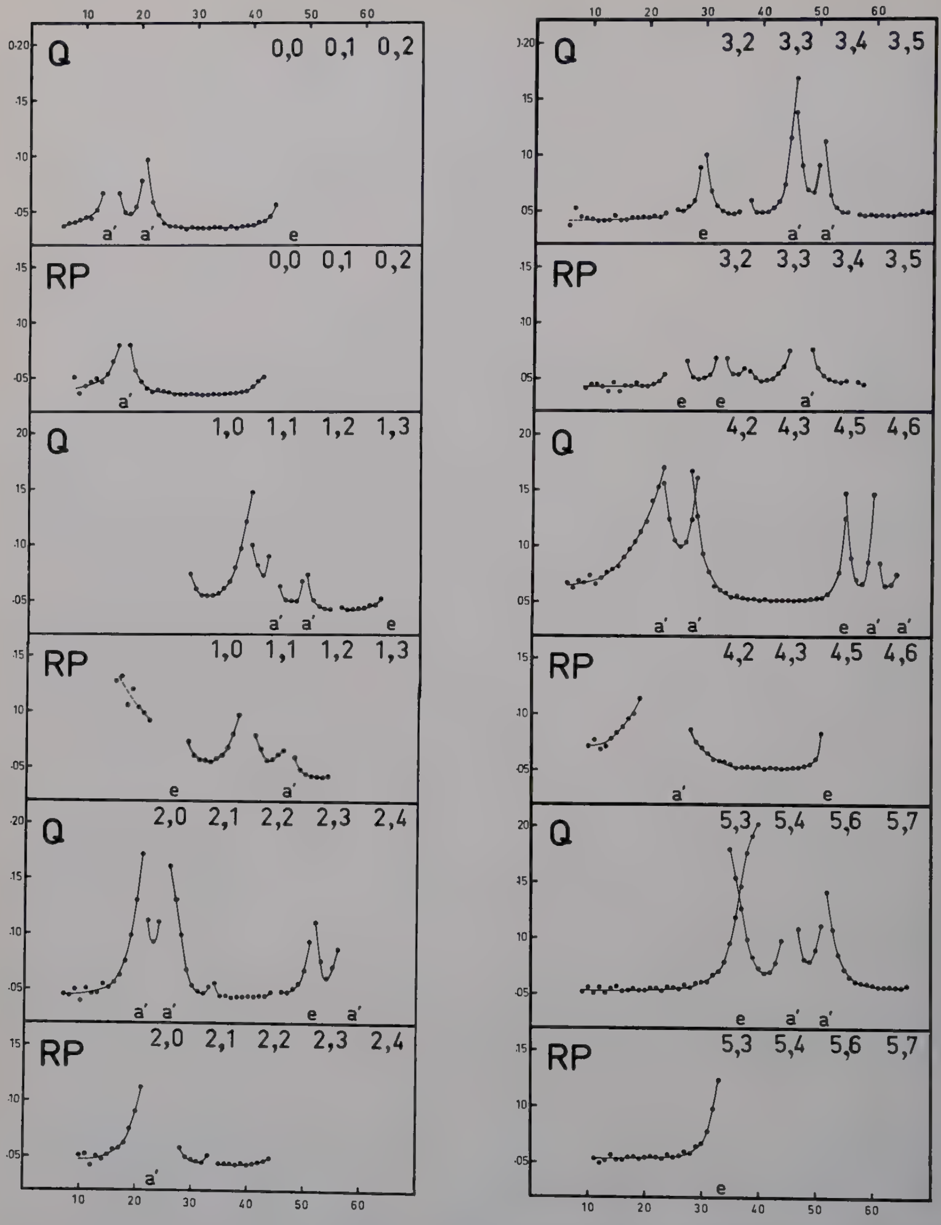

Fig. 2. $\Delta Q/2J$ and $\Delta RP/4J$ for the upper levels plotted against J. $^1\Pi\,^3\Sigma^+$ perturbations indicated with a', $^1\Pi\,^3\Sigma^-$ perturbations with e.

Table 9. Summary of perturbations.

v'	$J\,e\,{}^3\Sigma^-$			$J\,a'\,{}^3\Sigma^+$			J		v_p	B_p	$C_p + T_0(A\,{}^1\Pi)$
	RP	Q	RP	Q	RP	Q	RP	Q			
0				14.5	17	20.6			a'	0.585	38858
0	—	~47	—						e		39155
1	—	—	⩽28								
1							28	28			
1							39.5	39.5		0.60	40097
1				43.7	46.8	49.5			$a'+2$	0.572	40312
1								55			
1	—	~65	—						$e+2$		40575
2				21	~23	~27			$a'+3$	0.571	41003
2							33.5	33.5			
2							~45	45			
2	—	51.5	—						$e+3$		41341
2				~59	—	—			$a'+4$		
3	26	29.5	33						$e+5$	0.586	42056
3							~24	~24			
3							37.5	37.5			
3				45.7	47	50.7			$a'+5$	0.542	42396
3							~56	~56			
4				~23	~25	28.5			$a'+6$	0.540	43037
4	~52	55	—						$e+6$	0.571	43424
4				60	—	~65.5			$a'+7$	0.545	43740
5	33.5	36.7	—						$e+7$	0.5680	44096
5				45.7	—	52			$a'+8$	0.55	44368

$$\frac{Q(J-1)-Q(J)}{2J}=\frac{\Delta Q}{2J}=B''-B'-2J^2(D''-D')$$

$$\frac{R(J-2)-R(J-1)+P(J)-P(J+1)}{4J}=\frac{\Delta RP}{4J}=B''-B'+6D''-2J^2(D''-D').$$

The left-hand sides of these expressions were plotted against J. As the terms in $D''-D'$ are small the points lie on an almost horizontal line for unperturbed regions. At a perturbation the points deviate from these line. $\Delta Q/2J$ and $\Delta RP/4J$ diagrams for all upper levels are given in Fig. 2. For every v' level the points are the means of $\Delta Q/2J$ and $\Delta RP/4J$ respectively for all bands having the same v'.

Nature of the perturbing states

The diagrams in fig. 2 show that at some perturbations the intersection culminates at the same J value in the Q branch and in the R and P branches. At other perturbations, however, this is not the case. The former type of perturbation corresponds to interactions between the ${}^1\Pi$ state and singlets (${}^1\Pi$ or ${}^1\Delta$) or between the ${}^1\Pi$ state and triplets (${}^3\Pi$ or ${}^3\Delta$). The latter type corresponds to ${}^1\Pi\,{}^3\Sigma$ interactions.

A summary of all perturbations found is given in Table 9. Fig. 3 gives an energy scheme of the upper vibrational levels plotted against $J(J+1)$. Thick continuous lines indicate regions analyzed for Q as well as R and P lines, thick broken lines indicate

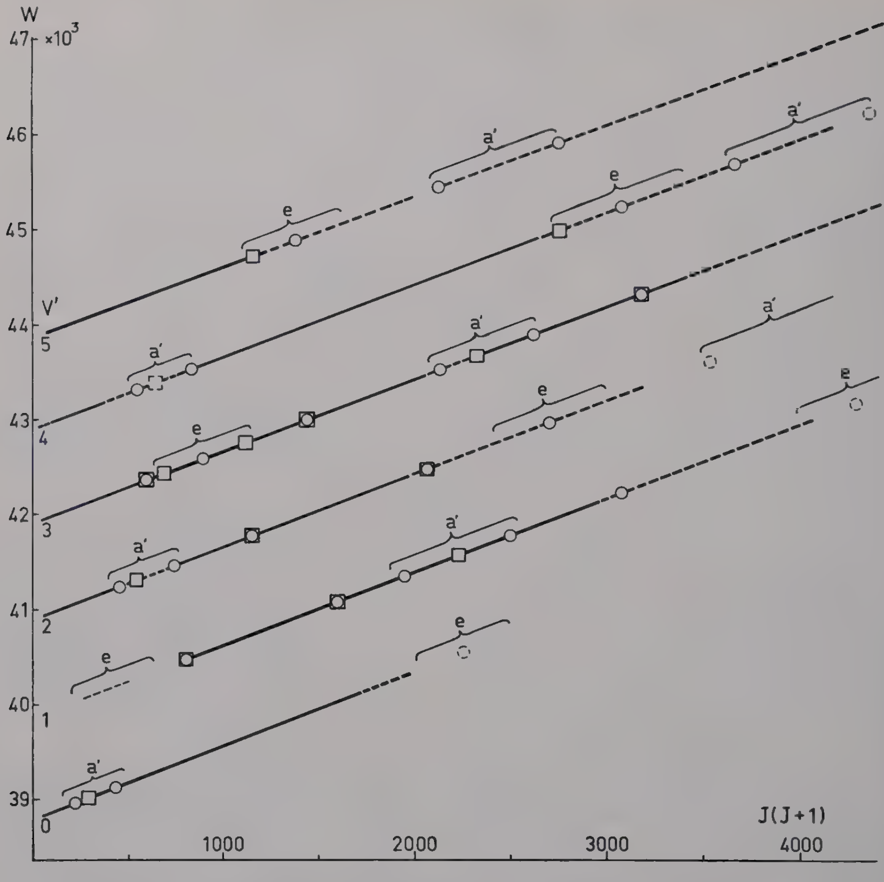

Fig. 3. Perturbations in the $A\,^1\Pi$ state of CS; term values plotted against $J(J+1)$. Thick lines: regions analyzed for Q and RP lines; thick broken lines: regions analyzed for Q lines only; thin broken line: region analyzed for RP lines. Circles indicate perturbations in the Q branches, squares perturbations in the RP branches. Dotted squares or circles indicate interactions not analyzed.

regions for Q lines only and thin broken lines regions analyzed for R and P lines only. Perturbations found in Q lines are marked with circles, perturbations found in R and P lines with suqares.

A $^1\Pi\,^3\Sigma^+$ interaction gives rise to three perturbations: one perturbation in the R and P branches at a certain J value and two in the Q branch, situated one at a higher and one at a lower J value than that for the R and P branches. A $^1\Pi\,^3\Sigma^-$ interaction is of opposite form.

Among the perturbing states one $^3\Sigma^+$ and one $^3\Sigma^-$ state are found. They are here called a' and e to conform with the states of CO. It has, however, not been possible to decide the nature of the other perturbing states. They are presumably $^1\Pi$, $^1\Delta$ or $^3\Pi$ states.

Determination of constants for the perturbing states

Eight $^1\Pi\,^3\Sigma^+$ interactions have been found. Owing to the lower intensity of the R and P branches and to the accumulation of R lines in the R head it was easier to follow the Q branches and to analyze them to higher rotational quantum numbers than the R and P branches. Thus for three $^1\Pi\,^3\Sigma^+$ interactions the analysis was carried out only for the Q branches. Fig. 2 shows that the perturbation at $J \sim 23$ in $v' = 4$ must arise from interactions between $^1\Pi$ and two perturbing states. One of these is $^3\Sigma^+$. That there must be two perturbing states here is apparent from the slopes of the two lines near the crossing point. The slope of the left-hand line is only about half that of the right-hand line (see Hultin and Lagerqvist 1951). Thus, near the intersection point there must be three curves. The spectrum is, however, so complicated in this region that it was impossible to find the corresponding lines with certainty. The rotational constants B_p of the perturbing states were determined in two ways. At two perturbations a sufficient number of extra lines were found to use the method given by Kovács, 1952. The culminations of all $^1\Pi\,^3\Sigma^+$ perturbations are found in the Q branches. Calling the corresponding J values J_1 and J_3 ($J_1 < J_3$), an approximate $B_{^3\Sigma^+}$ value can be obtained from the following expression (Lagerqvist and Uhler 1952)

$$B_{^3\Sigma^+} = B_\Pi \frac{J_3\,(J_3+1) - J_1\,(J_1+1)}{(J_3+1)\,(J_3+2) - (J_1-1)\,J_1}$$

The values of the energies, C_p, of the perturbing states at $J=0$, above $J=0$ in $v'\,(A\,^1\Pi)$ may be determined as follows. The terms of $^1\Pi$ and $^3\Sigma$ may be written approximately

$$F_J^\Pi \;= B_\Pi\, J\,(J+1),$$

$$F_{J+1}^{^3\Sigma} = C + B_{^3\Sigma}\,(J+1)\,(J+2),$$

$$F_J^{^3\Sigma} \;= C + B_{^3\Sigma}\, J\,(J+1),$$

$$F_{J-1}^{^3\Sigma} = C + B_{^3\Sigma}\,(J-1)\,J.$$

Since the J values J_1, J_2 and J_3 corresponding to the culmination points and the B values are known, the values of C may be calculated directly.

Six $^1\Pi e\,^3\Sigma^-$ perturbations have been observed through displacements in the Q branches. Only for one interaction—that in $v' = 3$—could the accompanying RP perturbations be analyzed. For the perturbation in level $v' = 5$ at $J \sim 37$ several extra lines were found, leading to an accurate determination of the corresponding value of $B_{^3\Sigma^-}$. The C value here was calculated from the relation given by Kovács, 1952.

Information about the perturbations is collected in Table 8. The following constants were derived for the perturbing states $a'\,^3\Sigma^+$ and $e\,^3\Sigma^-$. The lowest vibrational numbers are designated a' and e respectively.

$a'\,^3\Sigma^+$		$e\,^3\Sigma^-$	
$B_{a'+v}$	$= 0.585 - 0.008\,v$	B_{e+v}	$= 0.610 - 0.006\,v$
ω	$\geqslant 760$	ω	$\geqslant 750$
ωx	~ 7	ωx	~ 5
ν_0	$\leqslant 38858$	ν_0	$\leqslant 39155$

The magnitude of the perturbing matrix elements

It can be shown that the minimum distance between two interacting terms is $2H$, where H is the perturbing matrix element. If a sufficient number of extra lines is known H can be determined rather accurately. Thus for the $^1\Pi\,^3\Sigma^-$ perturbation in level $v' = 5$ at $J \sim 37$, $H = 16.1_5$ cm^{-1}.

A simple method to get an approximate value for H is to determine the slope η at the intersection point in the $B''-B'$ curve (Lagerqvist and Miescher 1958). We have

$$|\eta| = \left|\frac{\Delta B^2}{2H}(J+\tfrac{1}{2})\right|.$$

For the perturbation discussed here one obtains by this method $H = 17$ cm^{-1} in good agreement with the value given above. The other perturbations analysed have H values which are smaller or at most of about this magnitude.

5. Discussion

The foregoing rotational analysis establishes beyond doubt that the transition is $^1\Pi-^1\Sigma$. The bands have been observed in absorption using a variety of techniques, so that the lower state may be identified with $X\,^1\Sigma^+$, the ground state of the molecule. There remain for consideration two points:

(i) *The* $^1\Sigma-^1\Sigma$ *system of Crawford and Shurcliff*

This system is said to consist of four bands with single R and P branches: they form a v' progression and lie just to shorter wavelengths of the bands of the main system with $v' = 1$. The published analysis of these bands is certainly incorrect, for they also appear in absorption and therefore involve the ground state: however the value of B'' derived by Crawford and Shurcliff is considerably different from the value of $B''(X\,^1\Sigma^+)$. It may be that there is in fact no new transition here, but that rather the lines in question arise from transitions in $v' = 1$ of the main system. Indeed many of the lines in these regions have now been assigned to $v' = 1$, and the remaining unassigned lines may well arise from perturbed regions in $v' = 1$ which we have so far failed to analyze. Intensity variations from plate to plate support this conclusion.

Table 10. Summary of constants for CS.

State	T_0	ω_e	$\omega_e x_e$	B_e	α_e	r_e, Å
$A\,^1\Pi$	38798	1081.2_6	11.1	0.7799_5	0.0062_9[a]	1.574
$(?\,^1\Delta)$	$\leqslant 40097$	—	—	$\geqslant 0.60$		$\leqslant 1.80$
$e\,^3\Sigma^-$	$\leqslant 39155$	$\geqslant 750$	5	$\geqslant 0.610$	0.006	$\leqslant 1.78$
$a'\,^3\Sigma^+$	$\leqslant 38858$	$\geqslant 760$	7	$\geqslant 0.585$	0.008	$\leqslant 1.82$
$X\,^1\Sigma^+$	0	1285.08	6.46	0.82005[b]	0.00592[b]	1.535[b]

[a] $-0.0004_1(v+\tfrac{1}{2})^2$.

[b] From Mockler and Bird (1955).

Table 11. Electronic states of CO and CS.

State	CO			CS		
	T_0, ev.	ω'/ω''	B'/B''	T_0, ev.	ω'/ω''	B'/B''
$I\,^1\Sigma^-$	$\leqslant 8.23$	$\geqslant 0.48$	$\geqslant 0.75$			
$e\,^3\Sigma^-$	8.03	0.504	0.656	$\leqslant 4.85$	$\geqslant 0.58$	$\geqslant 0.74$
$d\,^3\Delta$?	7.66	0.524	0.653			
$a'\,^3\Sigma^+$	6.86	0.567	0.697	$\leqslant 4.82$	$\geqslant 0.59$	$\geqslant 0.71$
$A\,^1\Pi$	8.02	0.699	0.834	4.81	0.842	0.951
$a\,^3\Pi$	6.01	0.801	0.870			
$X\,^1\Sigma^+$	0	1.000	1.000	0	1.000	1.000

(ii) *The head at 2572.9 Å*

This is a weak head associated with the 0,0 band, only clearly recognizable in absorption: in emission the region is strongly overlapped by lines of the 5,4 band. Some at least of the lines may form part of the R branch perturbed to the violet at $J < 14$. It should be possible to clear up this point by a study of the absorption spectrum with high resolving power.

Constants for the electronic states of CS are collected in Table 10 and in Table 11 comparison is made with the low-lying states of CO (Mulliken 1958). The electronic configuration for the ground state of CS may be written.

$$\text{I.}\quad KKL(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2\ldots{}^1\Sigma^+.$$

The lowest excited configurations are expected to be

$$\text{II.}\quad \ldots(w\pi)^4(x\sigma)(v\pi)\ldots{}^1\Pi,{}^3\Pi,$$
$$\text{III.}\quad \ldots(w\pi)^3(x\sigma)^2(v\pi)\ldots{}^1\Sigma^+,{}^1\Sigma^-,{}^3\Sigma^+,{}^3\Sigma^-,{}^1\Delta,{}^3\Delta.$$

State $A\,^1\Pi$ may then reasonably be identified with the $^1\Pi$ state arising from II, and the states $a'\,^3\Sigma^+$, $e\,^3\Sigma^-$ with states arising from III. From configurations II and III there remain to be observed the $^3\Pi$, $^1\Sigma^+$, $^1\Sigma^-$ and $^3\Delta$ states, of which the $^3\Pi$ state presumably lies lowest.

The comparison with carbon monoxide reveals close similarities between the states of the two molecules, but the differences between the antibonding orbital $(v\pi)$ and the bonding orbitals $(x\sigma)$ and $(w\pi)$ seem to be smaller in CS than in CO, so that the excited states of CS are all, relative to the ground state, somewhat more stable than in the case of CO. This behaviour seems to be confined to CS and, perhaps, CSe, for the states of SiO and of SiS are much more nearly like those of CO (Lagerqvist and Uhler 1952).

A spectroscopic value for the dissociation energy of CS can be obtained only by a long and somewhat uncertain extrapolation of the vibrational levels in the ground state, giving $D_0'' = 181$ kcal/mole. For some molecules this method gives, as is well known, results subject to large errors. However, for the similar molecules SiO, GeO and SnO, the values of D_0'' obtained by Birge-Sponer extrapolations of the ground state levels are fairly close to the true values (Barrow and Rowlinson 1954). Thus we may conclude that the figure given above for D_0'' (CS) is probably not far wrong. This corresponds to $D_{298}'' = 182$ kcal/mole.

Schäfer and Wiedemeier (1958) have measured the standard heat of formation of gaseous carbon monosulphide by an equilibrium method: the first results indicate $Q_f \sim 60$ kcal/mole. If the heat of dissociation of diatomic sulphur is taken to be 83 kcal/mole (St. Pierre and Chipman 1954, Dewing and Richardson 1958), then $Q_f(S_{\text{gas}}) = 58.1_5$ kcal (Rossini *et al.* 1952), and, with $L_{\mathrm{C}} = 170.89$ kcal (Stull and Sinke 1956), $D''_{298}(\mathrm{CS}) = 169$ kcal/mole. If $D(S_2)$ is taken to be 101 kcal, then $\mathrm{D}''_{298}(\mathrm{CS})$ becomes 178 kcal/mole. It seems safe to conclude that $D''_{298}(\mathrm{CS}) = 175 \pm 7$ kcal. This fits well with the value of 186 kcal derived for the isoelectronic molecule SiO (Barrow and Rowlinson 1954).

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